

CHARACTERIZATION OF IRON MINERALS IN COAL BY LOW-FREQUENCY INFRARED SPECTROSCOPY

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The Bureau of Mines, U. S. Department of the Interior, is conducting basic research on minerals occurring in coal to assist in solving problems created by their presence. Of particular interest in these studies are the abundant iron-bearing minerals which are directly linked with air and water pollution, are important in coal combustion, carbonization and hydrogenation, and offer potential for profitable utilization. Iron is second only to aluminum as the most abundant metallic constituent of coal, reflecting its natural abundance in the crust of the earth. Iron is a major element of high-temperature coal ash and ranges from 5 to 35 weight-percent (reported as Fe_2O_3) for United States bituminous coals (1). Although some of the iron may be organically bound in the coal (2), a large portion is known to occur in a variety of mineral forms.

Previous studies have shown that one of the most effective methods for determining the structure and concentration of coal minerals is low-frequency infrared spectroscopy (3). The application of infrared analysis to a study of iron minerals in coal required a unique compilation of spectral data. Much of the required data was not available from the literature or was of such a poor quality as to be unreliable. In addition, most earlier work did not include the new and useful low-frequency data made available for most minerals by extension of high-resolution commercial infrared instrumentation to 200 cm^{-1} .

The purpose of this paper is to present the infrared data that we have collected for some iron-bearing minerals in bituminous coal, in both their original and altered forms, and to demonstrate the usefulness of this data for analysis of a variety of typical bituminous coal mineral samples. While iron minerals not included here may occur in coal, the iron minerals for this study were selected on the basis of their frequency of occurrence in samples examined at the Morgantown Coal Research Center and in coals described in the literature.

EXPERIMENTAL

To prepare the standard spectra required for this work, several specimens of each of the iron minerals were obtained from different localities. Milligram amounts of each of these samples were selected with a stereomicroscope under 10-60X magnification. As an aid in isolation of pure specimens, we made extensive use of microchemical and determinative mineralogy tests. The purities of specimens were verified from x-ray powder diffraction data and from infrared literature data, when available. These checks showed that many of the mineral samples had been incorrectly identified by the supplier. Several minerals were obtained as pure synthetic polycrystalline phases from Tem-Pres Research, Inc., State College, Pa., and infrared spectra of these synthetic minerals were used as further purity checks on natural mineral specimens.

Pellets for infrared analysis were prepared by hand blending one milligram of the preground mineral with 500 milligrams of powdered cesium iodide (Harshaw) for five minutes in a mullite mortar. This mixture was triple pressed in a die at 23,000 pounds total load, with a 15 minute total press time. Pellets were scanned immediately on a Perkin-Elmer 621 infrared grating spectrophotometer purged with dry air. Further considerations in solid state sampling of minerals for infrared analysis have been treated in an earlier publication (3). Coal minerals to be analyzed by infrared were enriched by a variety of techniques. Low-temperature ashing, under 150° C, in an oxygen plasma produced by an r.f. field of 13.56 MHz, for example, gave essentially unaltered mineral residues from coal. In addition, conventional gravity and magnetic separation methods and hand selection with a microscope were used.

RESULTS AND DISCUSSION

Sulfides. Iron disulfides, pyrite and marcasite (FeS_2), the most abundant iron-bearing minerals in coal, contain much reactive sulfur and thus are major contributors to air and water pollution. These dimorphs (cubic and orthorhombic, respectively) can be identified and differentiated by their infrared spectra in the low-frequency region only (3). Spectral differences, shown in Figure 1 and Table 1, were used to demonstrate that pyrite predominates in the bituminous coals investigated in this work. The detection and determination of pyrite by infrared spectroscopy has been helpful in research on methods for its removal from coal. Gravity separation methods are frequently employed and Figure 2 demonstrates the enrichment of pyrite in the 2.9 specific gravity sink fraction of a mine refuse sample from a West Virginia bituminous coal. The 1.7 specific gravity fraction, curve (a), is shown here to point out that absorption bands from other commonly occurring coal minerals, e.g., kaolinite, may overlap those of pyrite and thus decrease its detectability in mixtures not subjected to separation methods.

Pyrrhotite (Fe_{1-x}S) is an iron sulfide found in coal (4) and in coal ash slag, where it had been produced from the breakdown of pyrite (5). We did not detect infrared absorption bands out to 17 cm^{-1} for either the monoclinic or hexagonal crystalline forms of pyrrhotite, hence it is possible that this mineral cannot be determined in natural mixtures by infrared spectroscopy. We have not identified it in any of our bituminous coal samples examined to date by x-ray diffraction analysis.

The iron-bearing sulfide mineral, chalcopyrite (tetragonal, CuFeS_2), has been identified in coal (6, 7). It is known to be the most widely occurring copper mineral and is commonly associated with pyrite ores. Figure 3 and Table 1 show that its absorption bands are shifted to lower frequencies from the corresponding bands for pyrite. These data are in good agreement with those of Gillieson (8).

Carbonates. The carbonate mineral, siderite (FeCO_3), has been identified in coal and is believed to have been formed at the time of burial of plant remains (9). Weathering can convert it to limonite which can then lose water to produce hematite. Siderite has been identified in coals from wide geographic localities and varying ranks. Figure 4 demonstrates its detection in a Virginia bituminous coal. Here, siderite is seen to be the major constituent of a heavy sink fraction from fine coal washing. Adler (10) and Hunt (11) have presented the infrared

spectrum for siderite to 625 cm^{-1} and Angino (12) has published its infrared data only in the low-frequency region below 500 cm^{-1} . The distinction of siderite from other possible coal mineral carbonates was facilitated through use of the complete infrared spectrum, as shown in Figure 4, containing all relative intensity information.

Another common iron carbonate often found in coal is ankerite (6, 13, 14). Infrared data has been presented for ankerite by Huang (15) to 667 cm^{-1} and by Moenke (16) to 500 cm^{-1} . Both workers utilized very minor band shifts (3 to 5 cm^{-1}) for distinguishing ankerite from the isostructural members of its group, and attributed these shifts to cation substitution effects. In a recent study of the carbonate minerals in coal (17) we examined seven ankerite samples from different localities. We observed no detectable frequency shifts in the carbonate fundamentals from those of dolomite. In the low-frequency lattice vibration region, however, there was a general broadening of bands and other detectable changes. In going from dolomite to ankerite, the 252 cm^{-1} dolomite band was reduced in intensity, the 312 cm^{-1} band was reduced in intensity and shifted to higher frequency, and the 391 cm^{-1} shoulder was less resolved. This mineral was frequently misidentified by the supplier because five additional samples of ankerite that we examined were shown by infrared and x-ray analysis to be siderite.

Oxides and Hydrrous Oxides. The iron oxides, hematite and magnetite, and the hydrrous iron oxides goethite and lepidocrocite have all been identified in coal by petrographic or x-ray methods (18). These may occur in coal as original minerals or as products of weathering of iron-bearing minerals. Very little reliable infrared data is available in the literature for these oxides. Absorption bands for hematite, reported in the $1000\text{--}1110\text{ cm}^{-1}$ region by Hunt (11) and Omori (19), are in error, as none of the anhydrous oxides absorb above 600 cm^{-1} . The infrared spectrum of hematite presented by Liese (20) contains absorption bands due to an impurity, and our data indicate that his sample contained maghemite. Recently, infrared spectra for iron oxides, available as commercial chemicals, have been presented to 200 cm^{-1} by Afremow (21) and McDevitt (22). The spectra we obtained for naturally occurring mineral samples are only in partial agreement with the data in these two references. For example, the distinction between $\alpha\text{Fe}_2\text{O}_3$ (hematite, trigonal) and $\gamma\text{Fe}_2\text{O}_3$ (maghemite, cubic) is not readily apparent from the spectra presented in either paper. Our spectra for these dimorphs, Figure 5, show frequency differences for all three major absorption bands. These shifts were found to be consistent for several samples from different localities and are believed to be reliable. For magnetite (Fe_3O_4), Liese (20) reports (to 300 cm^{-1}) only one absorption band at 570 cm^{-1} for a number of naturally occurring magnetite specimens. Our magnetite spectrum, Figure 5, with two absorption bands, is in better agreement with that presented by Afremow (21) for the black iron oxide (Fe_3O_4). The conversion of magnetite through maghemite to hematite can be readily followed by use of their spectral differences, shown in Figure 5.

The iron oxide, wüstite (essentially FeO), is an alteration product of the iron minerals in coal, and has been found in coal ash slags and fly ash. The spectrum of a nonstoichiometric, single phase sample of synthetic wüstite exhibits only one broad absorption band at 375 cm^{-1} .

The titanium containing iron oxide, ilmenite (trigonal, FeTiO_3), which is frequently associated with hematite and magnetite, has been identified in coal (23). Titanium commonly occurs in United States bituminous coals (1), and shows a close correspondence to its natural abundance in the earth's crust. Hunt (11) and Omori (19) report infrared absorption bands for ilmenite in the region above 625 cm^{-1} which are undoubtedly in error. Liese (20) found three strong absorption bands, all in the low-frequency region, that differ as the Ti/Fe ratio varies. He shows these bands to shift systematically from 540, 461, and 325 cm^{-1} to 532, 440, and 295 cm^{-1} as Ti increases and Fe decreases. He points out that this frequency shift is not in the expected direction and suggests that the presence of intergrown hematite may be causing this effect. Data from our laboratory support his intergrowth interpretation. Our spectra for ten samples of ilmenite from various localities show consistent band positions at 525 (s), 438 (m), and $300\text{ (s)}\text{ cm}^{-1}$. Figure 6 shows the spectrum of a sample from Norway. This spectrum agrees better with Liese's set of lower frequency bands, while his set of higher frequency bands agrees better in frequency and shape with our hematite data.

Adler (24) and White (25) have shown that the hydrous oxide dimorphs goethite, $\alpha\text{FeO(OH)}$, and lepidocrocite, $\gamma\text{FeO(OH)}$, both orthorhombic, can be readily distinguished by differences in the $4000\text{--}600\text{ cm}^{-1}$ region. Figure 7 shows their marked spectral differences and presents additional data for the low-frequency region to 200 cm^{-1} . A further useful distinction between these dimorphs is their behavior on heating. Goethite dehydrates to form paramagnetic hematite while lepidocrocite dehydrates on heating to form ferromagnetic maghemite. We used these conversions for further verification of the spectra for all four forms. The absence of vibrations due to OH groups considerably simplifies the infrared spectrum, as shown by a comparison of Figures 5 and 7.

We have frequently identified the oxides of iron and their hydrous forms in samples obtained by magnetic separations from coal. For example, Figure 8 demonstrates the detection of substantial amounts of goethite in the magnetic fraction from a mine refuse sample from a West Virginia bituminous coal. The highly characteristic goethite bands at 800 and 900 cm^{-1} , assigned by White (25) to an OH bending vibration and an Fe-O stretching mode, respectively, are particularly useful because this doublet occurs in a range not extensively overlapped by bands of other common mineral components. Similarly, the weaker bands at 215, 358, and 1018 cm^{-1} , seen in the spectrum of the magnetic fraction in Figure 8, can be assigned to minor amounts of lepidocrocite. The capability of infrared spectroscopy for distinguishing between goethite and lepidocrocite can be applied to the determination of the mineralogical composition of limonite, $\text{FeO(OH)} \cdot x\text{H}_2\text{O}$, an amorphous mixture of hydrous iron oxides with variable water content that is difficult to characterize by x-ray diffraction. We have observed goethite to be the predominant species in several limonite specimens from a variety of world localities. Limonite has frequently been reported to be present in coal as a product of weathering.

Other types of coal product samples typically containing iron oxides as alteration products of original iron minerals are combustion products such as fly ash, boiler deposits, conventional high-temperature ash residues from coal, and burned mine refuse. Figure 9, curve (c), for example, demonstrates the extensive oxidation of pyrite to hematite in a sample of burned mine refuse from a West Virginia bituminous coal. The sample, obtained from a burning coal refuse bank, was

pulverized and subjected to float sink separations. The infrared spectrum of the 2.9 specific gravity sink fraction shows hematite to be predominant, with only minor amounts of pyrite remaining. This particular analysis demonstrates the necessity for using the low-frequency region, $600\text{--}200\text{ cm}^{-1}$, because there were no major absorptions above 600 cm^{-1} in the refuse sample. Comparison of curves (a) and (b) for pyrite and hematite shows that the specificity of their absorption bands affords an excellent opportunity for quantitative analysis and thus determination of degree of oxidation by burning or weathering.

$\text{Fe}(\text{OH})_3$, a hydrolysis product of ferric sulfates, known as "yellow boy," is frequently precipitated from alkaline streams containing drainage from coal mines. Although this compound exhibits a rather diffuse infrared spectrum, we have used its broad absorption bands centered at 450, 575, 675, and 3450 cm^{-1} for identification. We have been unable to find any infrared data to 200 cm^{-1} for this compound in the literature.

Sulfates. Iron sulfates occur in coals primarily as oxidation products of the iron sulfides, and various forms can be produced, depending on weathering conditions. Anhydrous FeSO_4 , or its various hydrates, can easily form and be converted by further oxidation into $\text{Fe}_2(\text{SO}_4)_3$ or any of its possible hydrates. Nufer (26), by x-ray diffraction, has determined that the species typically found in West Virginia bituminous coal are principally szomolnokite, $\text{FeSO}_4 \cdot \text{H}_2\text{O}$, and melanterite, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. Iron sulfates are associated with water pollution problems resulting from mine drainage, coal processing plants, and weathered refuse banks (27). The infrared spectra that we obtained for a number of samples from these sources showed different hydration states for the iron sulfates. For example, the surface film from a sample of coal mine refuse is seen from its infrared spectrum in Figure 10, curve (c), to be predominantly anhydrous iron sulfate, indicating oxidation in a very dry atmosphere. Minor amounts of the hydrated forms of ferrous sulfates and pyrite were also present in this sample. When considerable atmospheric moisture is present, the surface film on pyrite-rich mine refuse was usually identified as melanterite, as seen in Figure 11.

Hydrous iron sulfates are another class of minerals for which very little reliable infrared data is available in the literature. Adler (28) has presented the infrared spectrum of szomolnokite only to 800 cm^{-1} . Omori (29) has published poorly resolved infrared spectra for siderotil, $\text{FeSO}_4 \cdot 5\text{H}_2\text{O}$, melanterite, and coquimbite, $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, only to 600 cm^{-1} . Infrared data for the synthetically prepared forms of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ have been presented by Miller (30, 31) to 300 cm^{-1} and Sadtler (32) to 400 cm^{-1} . However, no systematic study has been made of the various hydrated sulfates of Fe^{2+} or Fe^{3+} showing the dependency of the infrared spectrum on additions of water to the crystal lattice. In the present work, infrared spectra were obtained for samples of naturally occurring and microscopically identified iron sulfate minerals. These included iron in both ferrous and ferric states and in the commonly found hydrated forms. The hydration states of some of these iron sulfate minerals are known to be easily altered (33). However, variations of temperature and relative humidity in our pellet preparation produced no detectable spectral changes. The spectral data for these minerals are shown in Tables 2 and 3, with their tentative vibrational assignments. In the absence of data for several intermediate hydrates, and the possibility of mixed crystalline phases for some samples, it was not possible to make any rigorous spectral-structural correlations. However, several spectral

differences among these minerals were observed and used in identifications. For example, the marked spectral differences allowing a distinction between anhydrous ferrous sulfate and one of its hydrated forms, melanterite, are shown in Figure 10, curve (b), and in Figure 11, curve (a). The weak OH absorptions appearing in the spectrum of the anhydrous form agree with those in the monohydrate and may be due to small amounts of this form.

Some systematic spectral variations were noted for lattice water vibrations. For example, the ferrous sulfate hydrate system (Table 2) showed the expected systematic increase in intensity of the OH stretching and HOH deformation modes with an increasing number of lattice water molecules. Absorption for ferrous sulfate hydrates in the OH stretching region showed two to four components, while absorption for ferric sulfate hydrates in this region was asymmetrically broadened to one band and generally shifted to lower frequencies. The frequency for the HOH deformation mode remained essentially independent of the amount of water present. It appeared near 1620 cm^{-1} (usually split) for the ferrous sulfate hydrates, but shifted to a higher frequency position near 1640 cm^{-1} for the ferric sulfate hydrates.

The fundamental vibrations of the sulfate ion, ν_1 , ν_3 , and ν_4 , as tentatively assigned in Tables 2 and 3 for iron sulfates, all indicate lower symmetry than that of the free tetrahedral ion. Ross (34) has discussed the reasons for lower symmetry of the sulfate ion in the solid state. When this occurs, degeneracies are removed and new selection rules allow forbidden vibrations to appear. For example, the degenerate ν_3 sulfate group vibration appears as a triplet in all samples examined. The ν_1 appears in all spectra, although it shows a substantially reduced intensity when just one water molecule is added. The frequency variations for the sulfate fundamentals are not systematic with additions of lattice water and changes in the oxidation state of the iron. However, the observed spectral variations for these iron sulfates, in spite of their irregularities, can be of diagnostic value and can provide a basis for identification of an individual compound.

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Table 1. - Infrared Absorption Bands for Common Iron Minerals

Mineral	Frequency, cm^{-1} ^a
Pyrite (Gilman, Eagle County, Colorado)	284 (w), 340 (m), 391 (vw), 411 (s)
Marcasite (Ottawa County, Oklahoma)	285 (w), 321 (m), 350 (m), 396 (s), 412 (s), 422 (vw)
Chalcopyrite (Messina, Transvaal, South Africa)	268 (w), 315 (m), 351 (s), 365 (sh)
Siderite (Washington, Connecticut)	~200 (w), 316 (s), 728 (m), 858 (m), 1410 (s)
Hematite (Ironton, Minnesota)	330 (s), 370 (sh), 470 (m), 550 (s)
Maghemite (LaCodosera, Badajoz, Spain)	320 (s), 451 (m), 530 (s)
Magnetite (Iron Mountain, Utah)	385 (s), 575 (s)
Wüstite (Synthetic, Tem-Pres Research, Inc.)	375 (s)
Ilmenite (Kragerö, Norway)	300 (s), 325 (sh), 438 (m), 525 (s), 675 (sh)
Goethite (Cary Mine, Ironwood, Gogebic County, Michigan)	248 (w), 280 (s), 385 (w), 402 (s), 450 (sh), 568 (m), 662 (w), 800 (m), 900 (m), 3095 (m), 3430 (b)
Lepidocrocite (Fellinghausen, Hessen, Germany)	215 (w), 275 (m), 358 (s), 480 (s), 740 (m), 1018 (m), ~3000 (b), ~3350 (b)

^a s = strong; m = medium; w = weak; sh = shoulder; b = broad.

Table 2. - Infrared Absorption Bands for Ferrous Sulfate Minerals, cm⁻¹

Tentative assignments	Anhydrous ferrous sulfate FeSO ₄ Orthorhombic Fisher Chem. Co.	Szomolnokite FeSO ₄ · H ₂ O Monoclinic Dividend, Utah	Rozenite FeSO ₄ · 4H ₂ O Monoclinic Ontario, Can.	Siderotil ^b FeSO ₄ · SH ₂ O Crystal system undetermined	Melanterite FeSO ₄ · 7H ₂ O Monoclinic Honshu, Japan
OH stretch, lattice water	3410 (w) 3250 (w)	3420 (m) 3240 (sh)	3430 (ms) 3250 (sh)	3448 (ms)	3530 (sh) 3455 (s) 3390 (sh) 3260 (sh)
HOH bend, lattice water	1490 (w)	1650 (w) 1620 (w) 1490 (w)	1620 (w) 1505 (w)	1622 (mw)	1650 (sh) 1618 (m)
Y ₃ , sulfate	1150 (s) 1135 (s) 1076 (m)	1165 (m) 1125 (s) 1095 (m)	1175 (sh) 1140 (s) 1100 (m)	1143 (sh) 1099 (s)	1140 (m) 1105 (s) 1085 (sh)
Y ₁ , sulfate	1010 (m)	1015 (m)	1020 (m)		988 (w)
	815 (m)	830 (mw)	860 (mw)	862 (w)	
Y ₄ , sulfate	660 (m) 618 (m) 595 (m)	660 (m) 620 (m) 599 (m)	670 (m) 627 (m) 607 (m)		605 (m)
	525 (m)	522 (m)	560 (m) 470 (w) 340 (w) 275 (m)		510 (w) 425 (w) 330 (w)
	290 (m) 270 (m) 210 (m)	290 (m) 270 (m) ~ 200 (m)			

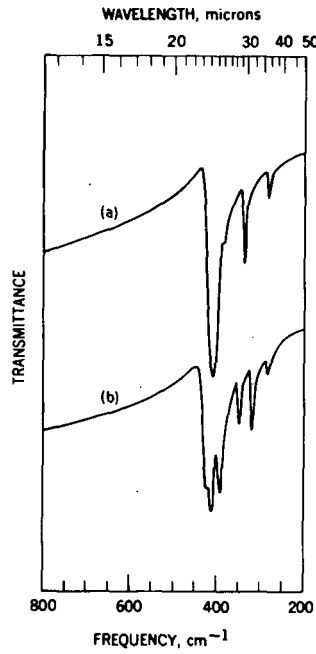
^a s = strong, m = medium, w = weak, sh = shoulder, b = broad.

^b Approximate values read from Omori and Kerr (see Ref. 29).

Table 3. - Infrared Absorption Bands for Ferric Sulfate Minerals, cm^{-1} ^a

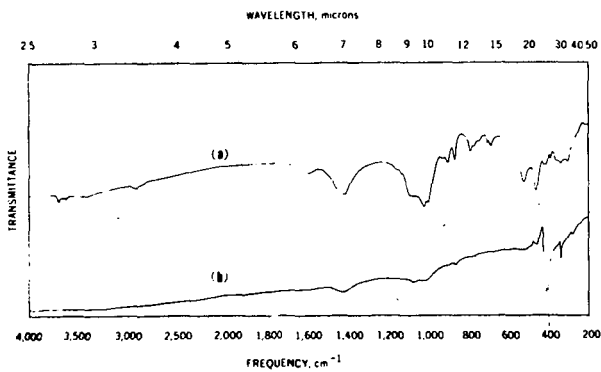
Tentative assignments	Kornelite $\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$ Monoclinic Inyo County, Cal.	Coquimbite $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ Hexagonal San Rafael Swell, Utah	Romerite $\text{Fe}_3(\text{SO}_4)_4 \cdot 14\text{H}_2\text{O}$ Triclinic Trinity County, Cal.	Ferric sulfate $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ J. T. Baker Chemical Co.
OH stretch, lattice water	3410 (s, b)	3300 (s, b)	3300 (s, b)	3360 (s, b), 3200 (sh)
HOH bend, lattice water	1640 (w)	1640 (w)	1640 (w)	1645 (m) 1610 (sh)
γ_3 , sulfate	1185 (sh) 1115 (s) 1050 (sh)	1165 (s) 1105 (s) 1065 (sh)	1129 (s) 1105 (s) 1085 (sh)	1150 (m) 1105 (s) 1052 (m)
		1023 (w)		
γ_1 , sulfate	990 (w)	1010 (w)	982 (w)	
	810 (w) 685 (w) 650 (w)	940 (w) 820 (w) 685 (w)	750 (w, b)	800 (w)
γ_4 , sulfate	595 (m)	608 (sh) 590 (m) 575 (sh)	626 (m) 605 (sh)	630 (sh) 595 (m)
	270 (w)	480 (w) 440 (w) 330 (w)	480 (w) 450 (w) 335 (w) 270 (w) 225 (w)	550 (m) 335 (w) 300 (w) 272 (w)

a s = strong; m = medium; w = weak; sh = shoulder; b = broad.



(a) Pyrite (Colorado)
(b) Marcasite (Oklahoma)

FIGURE 1. - Infrared Spectra for Iron Disulfide Dimorphs.



a. "Clay Fraction", 1.7 s.g. sink / kaolinite, quartz, calcite)
b. "Iron Fraction", 2.8 s.g. sink / pyrite

FIGURE 2. - Gravity Separation of Slurry Pond Refuse from a W. Va. Bituminous Coal.

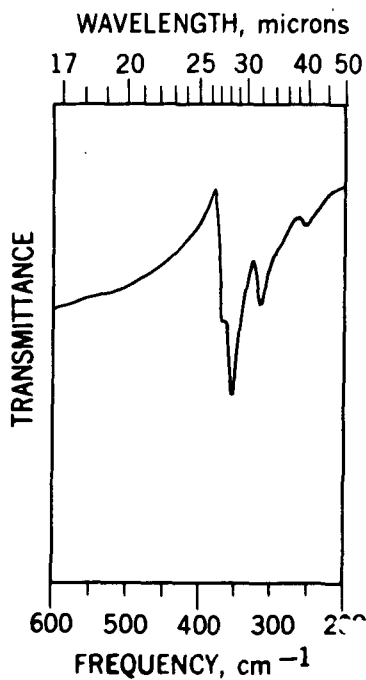
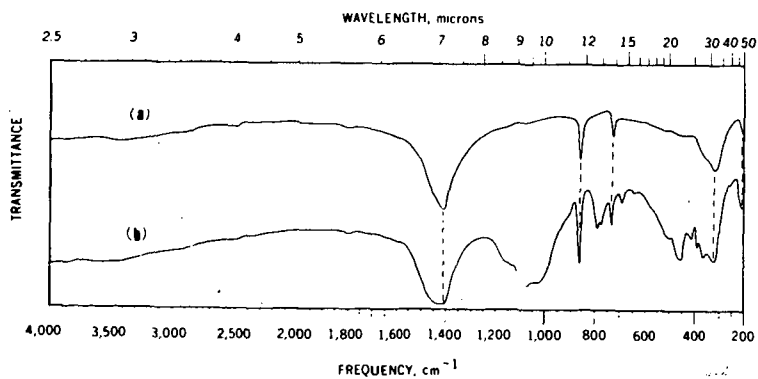


FIGURE 3. - Infrared Spectrum of Chalcopyrite from Messina, Transvaal, South Africa



- (a) Siderite (Connecticut)
- (b) Heavy sink fraction from the fine coal washing, 2.9 s.g. sink

FIGURE 4. - Identification of Siderite from a Virginia Bituminous Coal

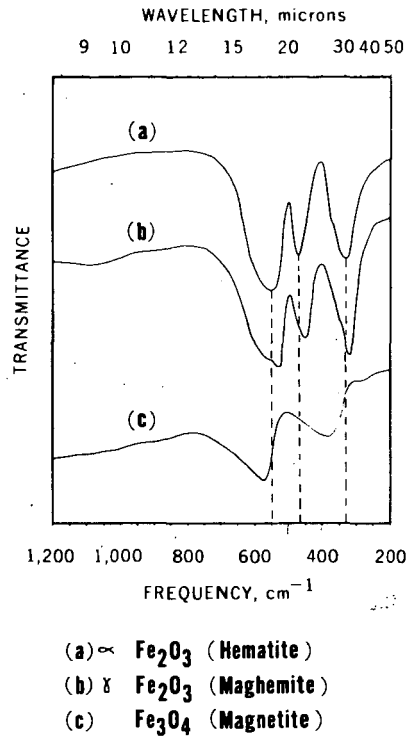


FIGURE 5. - Infrared Spectra of Iron Oxides

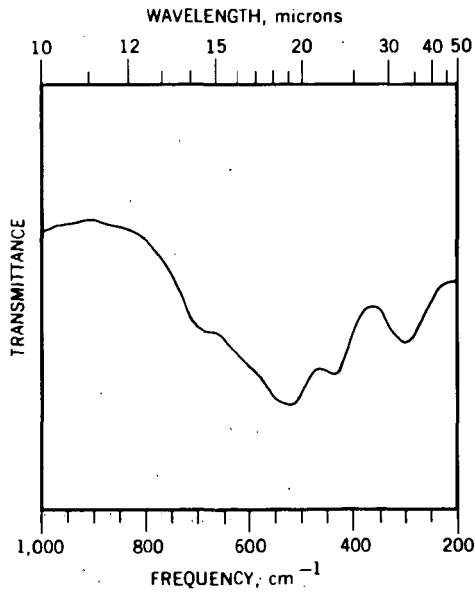


FIGURE 6. - Infrared Spectrum of Ilmenite (Norway)

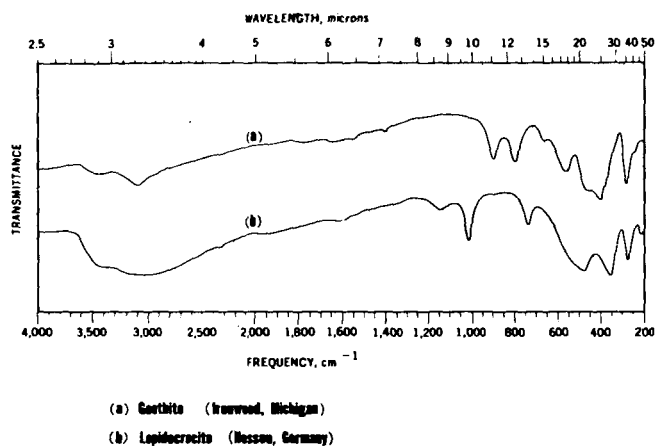


FIGURE 7. - Infrared Spectra of Hydrous Iron Oxide Polymorphs

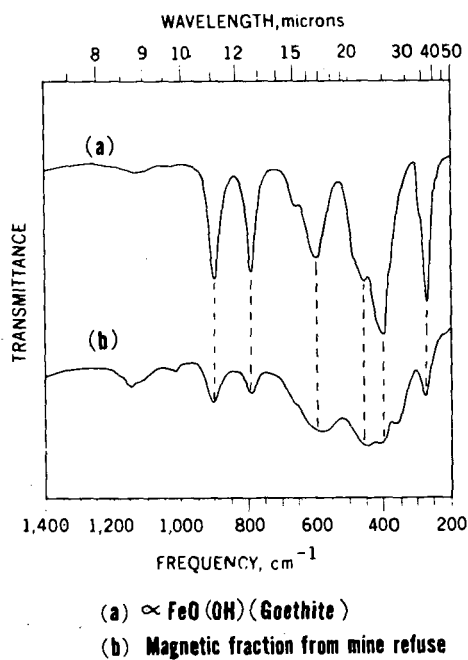
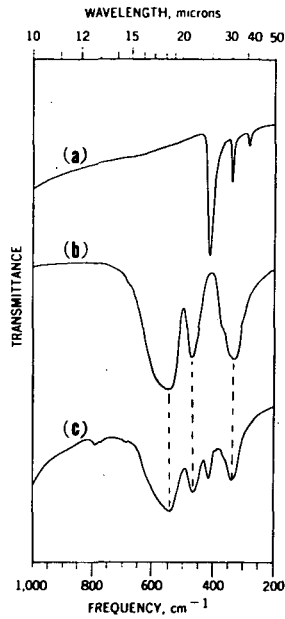


FIGURE 8. - Identification of Goethite in Mine Refuse from a W. Va. Bituminous Coal



- (a) Pyrite (Gilman, Colorado)
(b) Hematite (Iron-ton, Minnesota)
(c) Burned mine refuse

FIGURE 9. - Conversion of Pyrite to Hematite in Mine Refuse by Burning

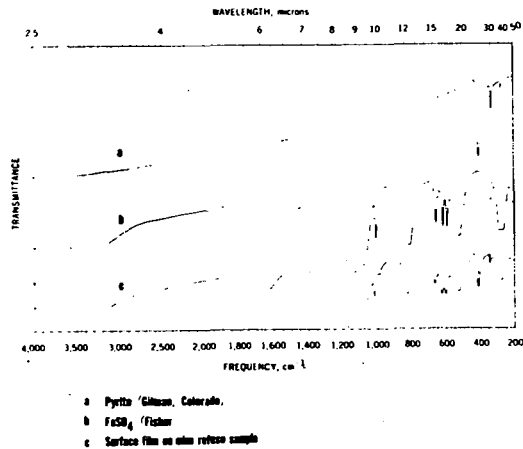


FIGURE 10. - Surface Oxidation of Pyrite from Coal Refuse in a Dry Atmosphere

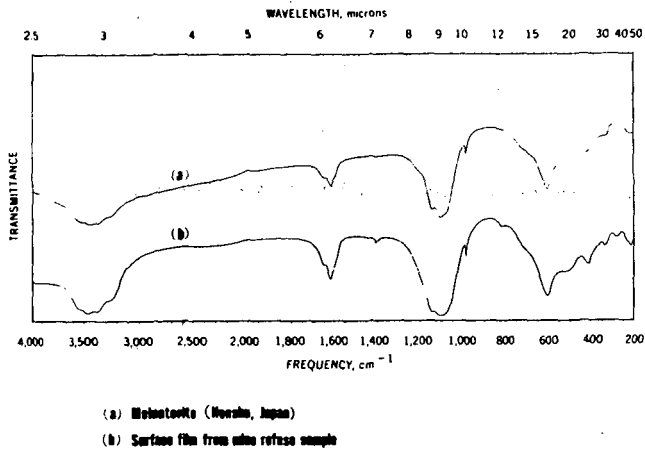


FIGURE 11. - Surface Oxidation of Mine Refuse in a Moist Atmosphere